INVESTIGATIONS OF INORGANIC-ORGANIC HYBRID PHOTODETECTOR

M.Tech. Thesis

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INVESTIGATIONS OF INORGANIC-ORGANIC HYBRID PHOTODETECTOR

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Technology

> by ANANYA TIWARI



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2018



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **INVESTIGATIONS OF INORGANIC- ORGANIC HYBRID PHOTODETECTOR** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from JULY 2016 to JUNE 2018 under the supervision of Dr. Vipul Singh, Associate Professor, Discipline of Electrical Engineering, Indian Institute of Technology Indore, India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Ananya Tiwari

Dedicated to my loving Grandparents

"AMMA &PAPPA"

Abstract

Metal oxide nanostructures have been utilized as suitable candidates for optoelectronic applications as they are chemically and thermally stable, provide larger surface to volume ratio for better interaction with their environment. Among them, ZnO is attractive material because of its capability of showing morphological diversity. Different nanostructures with varying aspect ratios, morphology have been investigated. In this work, ZnO Nanostructures (ZN_S) were synthesized over ITO coated glass substrate by hydrothermal technique using Zinc nitrate and Hexamethylenetetramine solution with in situ addition of Potassium Permanganate (KMnO₄). On varying the precursor concentrations during hydrothermal growth, change in morphological structures from Nanorods to Nanopencils and Nanoplates have been observed. It is demonstrated that the KMnO₄ concentration has great influence on morphology and on the alignment of ZnO Nanostructures. Effect of KMnO₄ on the optoelectronic properties of the grown nanostructures has also been analyzed. High aspect ratio is desired as material properties depend closely on it, thus, ordered Nanostructures are expected to enhance performance of various technologically important devices like Light emitting diodes, Solar cells, Biosensors and Photodetectors. The Bilayered Hybrid detector consisted of ZNs coated with a layer of π -conjugated polymer viz. MDMO-PPV. The working device is sensitive towards visible spectrum of light (λ =490nm). The detailed mechanism of growth of ZN_S along with its overall influence on response of resulting Hybrid Photodetector will be discussed in detail in our work. The highlight of the work is enhanced performance of our ZnO/MDMO-PPV hybrid device with a significantly high rectification ratio of 466, highest photosensitivity obtained around 6923 and Photoresponsivity of 3.7A/W at -12V under an incident light with wavelength 490 nm.

LIST OF PUBLICATIONS

 Delivered a short invited talk on "Hydrothermal Growth of ZnO Nanostructures towards Hybrid Photodetector Applications" in the 3rd International conference on Nanomaterials (ICN 2018) held on 11-13 May'18. Secured second position in the same.

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NOMENCLATURE

	λ	Wavelength
	Ag	Silver
	$\mathbf{E}_{\mathbf{g}}$	Bandgap
	I-V	Current-Voltage
	K _B	Boltzmann's Constant
	KMnO ₄	Potassium Permanganate
	MDMO-PPV	Poly [2-methoxy-5-(3',
7'dimethyloctyloxy)		
		1, 4-phenylenevinylene]
	ZnO	Zinc Oxide
	НМТА	Hexamethylenetetramine
	Zn(NO ₃)2.6H ₂ O	Zinc nitrate hexahydrate

ACRONYMS

НОМО	Highest Occupied Molecular Orbital	
LUMO	Lowest Unoccupied Molecular Orbital	
PL	Photoluminescence	
FESEM	Field Emission Scanning Electron Microscope	
PVD	Physical Vapour Deposition	
XRD	X-Ray Diffraction	
UV-Vis	Ultra Violet - Visible	

Chapter 1

Introduction

Semiconductor devices are found in a myriad of technological applications starting from small and simple devices like electronic timer to highly advanced and sophisticated machines like medical instruments, computer, etc. Optoelectronics has become an important part of our lives. Whenever light is used to transmit information, tiny semiconductor devices are needed to transfer optical signals into light currents and vice versa. That is why, in today's world, Photodetectors are one of the most prevalent devices and they are widely used in areas of commerce, industry, entertainment, research and other various technological applications [1-2]. There is a growing need for large area, user friendly, inexpensive, integrated optical sensors so that they can be integrated into many novel applications such as wearable electronics, implantable biomedical devices etc [3]. To meet such demands, silicon industry emerged; later organic semiconductors gained increased scientific and industrial interest in the last decade as an alternative to traditional solid-state solutions. Recent researchers have drawn their attention towards hybrid inorganic organic devices due to the fact that they combine merits of both organic and inorganic components to meet the ever rising performance requirements [4]. This work primarily focuses towards the development of ZnO/MDMO-PPV based hybrid Photodetector. As inorganic and organic semiconductor play a major role in these devices, the fundamentals for understanding the principles are dealt within this chapter.

1.1 Photodetector: A brief description

Photodetector or photo-sensor is a sensor of light which converts light photons into electrical energy proportional to incident light intensity. Solid state photodetectors are mainly used as optical sensors which convert incident light signal into either current or voltage signal. Some examples of the solid state based photodetectors are Schottky diodes, quantum well infrared photodiodes, superconducting tunnel junction (STJ) and semiconductor photodiodes [5]. Commercially available photodetectors with illumination window are shown in Figure 1.1



Figure 1.1 Commercially available Photodetectors

1.1.1 Commercial Applications

Photodetectors have applications in various fields like military, medical science, scientific research, space, traffic, consumer electronics etc. Few of the most common applications of the photodetectors can be listed as color sensor element for digital camera, automatic traffic lighting controls, fiber-optic communication systems, optical scanners, photography, security screening, machine vision, wireless LAN, remote control devices, industrial automation and many other endeavors [6-7]. Photodetectors are also widely used in scientific research, such as particle detectors and photomultipliers for photon detection. Image sensors are another important application of photodetectors; the most used image sensors are digital charge-coupled device (CCD) and complementary metal-oxide-semiconductor (CMOS) active pixel Sensors [8]. Some examples of photodetectors that sense light by converting light energy to other energies are bolometer which measure electromagnetic radiation by means of heating the material and radiometer which measure electromagnetic radiation by sensing light pressure [9]. Figure 1.2 shows few commercial applications of photodetectors.



Figure 1.2 some commercial applications of photodetectors

1.1.2 Fundamental Working Principle of Photodetector

The basic working principle behind photo detection process is that when light falls on the surface of a semiconductor material, it gets absorbed if the energy of the incident photons $(E_{ph}=hc/\lambda)$ exceeds the energy band gap of the material (E_g) . This absorption generates an electron hole pair for each photon absorbed, electron is excited from the band to the conduction band and in result a hole is generated in the valence band as shown in Figure 1.3. These generated electron hole pair separates and drifts to the respective electrodes under intrinsic or externally-applied electric field. This carrier drift gives rise to the photocurrent in the external circuit which is directly proportional to the amount of light incident.



Figure 1.3 a) Exciton generation in semiconductors b) Spectrum of light

1.2 Inorganic Semiconductors

It is a semiconductor material which has an electrical conductivity value falling between that of a conductor, such as copper, gold etc. and an insulator, such as glass. The energy band diagram of the materials is shown in Figure 1.4. The two energy bands are the valence band and the conduction band. These bands are separated by a region which designates energies that the electrons in the solid cannot possess. This region is called the forbidden gap, or bandgap Eg. In semiconductors there is a small energy band gap (1-3eV) between the valence and conduction bands. Their resistance decreases as their temperature increases, which is behavior opposite to that of a metal. Their conducting properties may be altered in useful ways by the deliberate, controlled introduction of impurities ("doping") into the crystal structure. The conductivity of semiconductor materials can be varied by doing changes in temperature, optical excitation, and impurity content.



Figure 1.4 Energy band diagrams of metal, semiconductor and insulator

Semiconductors can be classified as elemental semiconductors, found in group IV of the periodic table and compound semiconductors formed from the combination of group III - V elements and group II - VI elements. In elemental semiconductors each atom such as or is bonded with neighboring atoms of the same type, forming a covalent bond. Compound semiconductors composed of two or more elements in a certain ratio. Si and Ge are the most commonly used elemental semiconductors and some examples of compound

semiconductors are a GaAs, InP and ZnO [10]. Si is the most widely used intrinsic semiconductor material. It is a tetravalent semiconductor i.e. it has four electrons in its outer shell. Atoms in Si are linked together to form an ordered crystal structure called the diamond structure (Figure 1.5). Inherently Si is an intrinsic semiconductor with no impurities added where as in order to vary the conductivity of the semiconductor the impurities are purposely introduced into the semiconductor crystal via doping technique [5].



Figure 1.5 Covalent bonding in Si

Heavily doped semiconductors are more conductive and thus have less resistance. Diffusion of impurity atoms from elements of column III and V of the periodic table form p-type (mostly holes) and n-type (mostly electrons) doped or extrinsic semiconductors respectively. In an intrinsic semiconductor there are no additional energy levels present within the band gap region where as additional levels are introduced in the energy band structure, usually within the band gap due lattice defects present in the extrinsic semiconductors as shown in Figure 1.6. [11]



Figure 1.6 Energy band diagrams of intrinsic and extrinsic semiconductors

1.2.1 Charge Transport in Inorganic Semiconductors

In inorganic semiconducting materials, charge transport occurs through wave-like propagation of carriers in well-established conduction or valance bands, with occasional scattering of carriers at impurity sites, lattice dislocations or interactions with phonons. Therefore in these materials, mobilities can reach large values, ranging from 10^{-3} cm²V⁻¹s¹ to 10^{3} cm²V⁻¹s⁻¹. The mobility of charge carriers determines the transport in semiconductors. The electrons in the conduction band are relatively free to move, but bound by the periodic potential of the lattice nuclei. Thus the effective mass is different from that of a free electron. The energy-momentum relationship of a conduction electron can be written as

$$E = P^2 / 2m_e \tag{1.1}$$

Where, p is the crystal momentum and m_e is the effective mass of electron. If a charge experiences a force (e.g. an electric field), the carrier is forced to move with its mobility accordingly to the force. The classical transport model of Drude defines the mobility in semiconductor as:

$$V_D = \mu E \tag{1.2}$$

$$\mu = t_c / m^* \tag{1.3}$$

 V_D is the drift velocity, E the electric field and μ is the mobility. Furthermore, the mobility depends on the charge of the species q; t_c is the relaxation time i.e. the mean

time between scattering or collision events and it depends inversely on the effective mass m^* . The conductivity σ expresses the ability of semiconductor to conduct current. It is proportional to the product of mobility and carrier concentration. The conductivity of a material is therefore given by:

$$\sigma = qn\mu_n + qp\mu_p \tag{1.4}$$

With electron density n, hole density p, electron mobility μ_n and hole mobility μ_p [5, 11].

Types of Inorganic Photodetectors

Inorganic Photodetectors can be classified as photoconductors, photodiodes and phototransistors. Some of the Photodetectors are discussed briefly:

Photoconductor: The simplest type of Photodetector is a photoconductor. These are usually metals that form an ohmic contact with the semiconductor. When light falls on the semiconductor material, excess carries are generated, that form the current. It is a light-dependent resistor for which conductivity changes with the change intensity of the incident light [5]. The schematic of the photoconductor device is shown in figure 1.7(a).

Photodiodes: A photodiode is based on a simple pn or pin junction. In the case of the pn junction diode, carriers are generated in the depletion region. By applying a high reverse bias, the generated electrons and holes are separated and the current is measured. The disadvantage of the pn junction photodiode is that the depletion width is small and depends on the doping concentrations in the semiconductor. It is not possible to tailor the depletion region over a wide range. This can be overcome by using the pin photodiode, which is a special case of the pn junction photodiode. The schematic of the photodiodes is shown in figure 1.7[(b)-(c)]. The carriers are generated in the intrinsic region and then extracted by application of reverse bias. Electrons that are generated move to the n side, while holes move to the p side. The advantage of the pin structure is that the quantum efficiency, sensitivity, and gain of the device can be controlled by the thickness of the intrinsic region while a thin p and n regions can be maintained [12].

Phototransistor: The phototransistor uses the transistor gain action in conjunction with the carrier generation due to light absorption. The transistor has a large base area (lightly doped) to collect the photons, at the base and collector depletion region. This is unlike a conventional BJT, where the base is usually thin to prevent carrier loss due to recombination (when the carriers move from emitter to collector). This accumulation of carriers at the base lowers the potential and increases the efficiency of transfer of carriers from the emitter to the collector. Instead of a regular transistor, a heterojunction transistor can also be used. The emitter material has a larger band gap than the base, to minimize absorption [12]. Schematic is shown in Figure 1.7(d).



Figure 1.7 Types of Inorganic Photodetectors

1.2.2 Challenges

Although inorganic crystalline semiconductor based photodetectors have shown high performance but it still requires very precise processing under highly demanding conditions that calls for high cost. Current scenario looks out for innovative applications of photodetectors like system embedded in textiles and smart food packages, requiring fully flexible structures, relatively low voltage operations and low technology cost which are not possible for silicon based devices. Silicon is found to be unsuitable for such applications because the maximum area possible till date with the silicon as substrate is 12" in diameter where as polymer thin films can very well be coated on infinitely long flexible plastic sheets and glass substrates [13].

1.3 Organic Semiconductors

Organic semiconductors are carbon based materials having alternative double and single bonds in their backbone. The semiconducting properties of these materials are due to these alternative double and single bonds. The backbone carbon for these materials is sp^2 $+p_z$ hybridized state [14]. Three sp^2 hybridized orbital form three strong covalent sigma bonds with neighboring atoms giving mechanical strength to molecular structure. The remaining p_z orbital of each carbon atom, which lie perpendicular to the plane of sigma bonds, form additional weak bonds with neighboring p_z orbital known as π bonds of alternate carbon-carbon single and double bonds is known as π conjugation and organic compounds with π conjugation in their structure are known as π conjugated organic materials. Sigma bonds lie deep in energy and hence very difficult to make use of them for practical applications. Instead, π bonds are very weak and due their weak nature the electrons forming π bonds (π electrons) remain delocalized over the backbone of the molecular structure. These delocalized π electrons over the plane of molecular structure are essentially responsible for semiconducting nature in these materials [14]. Typical examples of π -conjugation in small molecules and polymers are shown in Figure 1.8. Band gap is reduced due to extension of delocalization length. Generally, band gap between HOMO and LUMO is 1.5eV-3.5eV causing strong absorption in near UV and visible region. Thin films of small molecules are prepared by thermal evaporation while drop casting, spin coating, printing, doctor blade etc are adopted for fabricating thin films of polymer materials. Organic semiconductors find its applications in new niche markets of flat and flexible electronics, stable sensors, electronic artificial skins; smart fabrics; radio-frequency identification and e-heath monitors implanted under skin.



Figure 1.8 Structures of some π conjugated materials

(a)N, N'-diphenyl-N, N'-bis (3-methylphenyl)-[1.1'-bi-phenyl]-4, 4' diamine (TPD) (b) Tris (8- Hydroxyquinolinato) aluminum (Alq3) (c) Poly (p-phenylene vinylene) (PPV) (d) Poly (9-Vinylcarbazole) (PVK)

As the demand of electronic devices holding new and novel functionalities that are not achievable using the traditional silicon technology is increasing, organic semiconductors are replacing traditional inorganic materials used in sensors, displays, transistors, diodes, and photovoltaic [15]. Some applications of organic electronic devices are shown in Figure 1.9.



Figure 1.9 Applications of Organic devices

We can distinguish two main classes of organic semiconductors on the basis of their molecular weight and basic units: small molecule and polymers. Figure 1.10 summarizes the examples of different types of organic semiconductors.

Small molecules: The small molecules have monomer units less than '10' and have low molecular weight organic compounds (< 1000 g/mol) in which carbon atoms form molecules usually with benzene rings.

Polymers: Polymers have monomer units greater than '20' in numbers and are high molecular weight organic compounds (> 1000 g/mol) comprising of many linked small repeating units, called monomers. Polymers can further be classified as homopolymer which is made of a single monomer and a copolymer which consist of two or more monomers.



Figure 1.10 Classifications of Organic Semiconductors

1.3.1 Charge Transport in Organic Semiconductors

Due to the presence of disorder along with the weak Vander Waals force of interaction the charge transport in these materials occurs by the means of hopping among localized states, which results in low charge carrier mobility. Hopping conduction can be understood as the redox reaction between two molecules as shown in figure 1.9.



Figure 1.11 Schematic of charge (hole) hopping between transport sites

Measurement of mobility as a function of various parameters like temperature, electric field, concentration etc is one of the most widely adopted methodology to understand the charge transport behavior in organic semiconductors. Generally, mobility is assumed to be drift mobility except at very low applied electric field where the diffusion governs the charge transport. Various models have been proposed to describe the charge transport and dependence of mobility on various parameters, out of which the most successful model was Gaussian disorder model (GDM), which adopted for analyzing the charge transport studies in this report, is explained below:

Gaussian Disorder Model:

Gaussian disorder model (GDM) was proposed by Bassler and co-workers in early 1980s. In GDM it is assumed that charge transport in organic semiconductor occurs by the means of hopping of charge carriers among localized states which have both positional and energetic disorder. Energetic disorder is due to dipolar interaction between molecules and surrounding and positional disorder is due to spatial and structural randomness of transporting sites [16]. In this model the transporting site energies; i.e. is the density of states (DOS) is decided by Gaussian distribution function as in eq (1.5).

$$\boldsymbol{\rho}(\boldsymbol{\epsilon}) = \frac{1}{\sqrt{2\pi\sigma^2}} \boldsymbol{e}^{\left(-\boldsymbol{\epsilon}^2 \middle| \boldsymbol{2\sigma}^2\right)}$$

(1.5)



Figure 1.12 Schematic of Gaussian disorder due to charge hopping

Where σ is the standard deviation of DOS. This assumption is justified by the dependence of DOS on large number of randomly varying co-ordinates and the observation of Gaussian shape for absorption and fluorescence bands for disordered organic solids [16].

1.3.2 Challenges

Organic photodetectors have many advantages but unfortunately, it suffers from few drawbacks such as their efficiency is still lower than the required demand. Mostly organic semiconductors were found to exhibit p-type conductivity, which challenged researchers to develop n-type organic semiconductors. Most commonly used high performance bulk heterojunction are formed from the blend of P3HT and fullerenes (such as PCBM) as a donor and acceptor material respectively. The performance of these devices is limited because of electron acceptor materials such as PCBM, as they have low electron mobility, have instabilities against oxidation and reduction, poor electronic tunability, very weak absorption of visible light, decreasing the volume fraction occupied by the strongly absorbing electron donor material.

1.4 Hybrid Photodetectors

The potential for new technological opportunities and reduced product cost has fueled recent efforts to replace crystalline silicon as the active component in many electronic devices. New approaches for inorganic-organic hybrid devices broadened the application opportunities of organic optoelectronic devices. Organic-inorganic hybrid devices are fabricated by the nano or molecular-level interactions between organic and inorganic materials. In particular, combination of organic polymers with inorganic nanostructure materials allows the construction of flexible and sophisticated organic-inorganic devices. The short life and low efficiency of organic photodetectors act as a barrier to make them commercially available. Recent research has suggested that in order to improve the performance of low-cost, flexible photodetectors the following areas should be addressed vis-a-vis introducing new materials with higher charge mobilities and controlled morphology to generate optimal interfacial area for Exciton dissociation while maintaining a bi-continuous structure allowing percolation of the separated charges to the collecting electrodes. Hybrid Photodetectors combine the unique properties of nanostructure inorganic semiconductors Such as TiO₂, ZnO, with film-forming properties of conjugated polymers as MDMO-PPV, P3HT. One extensively studied material system among the nano crystal-polymer blends is zinc oxide (ZnO). Zinc oxide is a promising semiconductor for use in optoelectronic devices due to high electron mobilities, and solubility in organic solvents. The nano structured ZnO with controllable morphology can be synthesized by a hydrothermal method on conducting glass or plastic substrates [17, 18].

1.4.1 Hybrid Photodetector Architecture and Operation

Photodetector has been studied for over decades now. The simplest design that came into picture was single layer photodetector in which active layer was sandwiched between two conducting electrodes. This design suffered from the problem of recombination of charge carriers. To address this problem, another architecture was designed having a donor material and an acceptor material, both stacked together with the electrodes in a planar structure. This was called bilayered or planar Photodetector. Problem of recombination

was reduced as donor-acceptor interface area was available for the charge carriers to dissociate before they could recombine but still recombination was persistent because of traps and defects. Next architecture was bulk heterojunction photodetector which was designed with the aim to blend the acceptor and donor material intimately so that large donor-acceptor interface area was readily available for exciton dissociation. However, such architectures need large enough domain size so that acceptor material should be in contact with other electrodes and donor material should be in contact with other electrode for efficient charge transport as shown in figure 1.13.



Figure 1.13 Different photodetector architectures: a) Single layer photodetector b) Bilayered or planar photodetector c) Bulk heterojunction photodetector

Bulk heterojunction photodetectors are more sensitive towards nanostructured materials as they not only provide large interface area for exciton dissociation but also efficient charge transport to respective electrodes. Our design focuses on nanostructures as acceptor material. The hybrid photodetectors focus on novel concepts towards more efficient photodetectors using both organic and inorganic materials. State-of-the-art hybrid photodetectors mostly comprises of low band gap metal oxide inorganic materials such as CdSe; TiO₂; Bi₂S₃; MoO₃ ; ZnO as electron acceptors and organic materials such as MDMO-PPV, MEH-PPV, P3HT, P3DDT as electron donors. The device architecture of hybrid photodetectors incorporating ZnO nanorods is schematically shown in Figure 1.14. The ZnO/MDMO-PPV device form ordered bulk Heterostructures. The electron mobility of organic semiconductors is typically several orders of magnitude below the

hole mobility of inorganic semiconductors. In hybrid Photodetector the nanostructured inorganic semiconductor (e.g. ZnO) plays an active role as electron acceptor. The photons are absorbed in the organic absorber material (e.g. MDMO-PPV) generating excitons. These excitons require a nearby interface of the electron accepting material in order to be dissociated into free carriers. The small Exciton diffusion length (20nm) in the organic semiconductor thus requires a dense array of nanorods for efficient Exciton dissociation and generation of photocurrent.



Figure 1.14 Schematic of Hybrid Photodetector

1.4 Objectives of this Work

The main objective of this work is the development and analysis of possibilities to extend the efficiency of hybrid photodetector by preserving the advantages of soluble organic polymers under the perspective of industrial applications. Focus of the work is the modification and investigation of the photoactive layer and their application in photo detection devices. This work for hybrid photodetector is centered on MDMO-PPV as conjugated organic polymers and ZnO as an inorganic semiconductor. The highlights of this work are as follows: 1. Optimization and integration of hydrothermally grown ZnO nanostructures that serves as a promising technique for high performance ZnO/MDMO-PPV Bilayered photodetector applications.

1.5 Organization of the Thesis

Chapter 1 describes the detailed discussion of inorganic and organic semiconductors. Hybrid photodetector as main critical application of inorganic-organic semiconductors has been discussed also; the main theme of research work presented in this thesis has been discussed.

Chapter 2 describes the work done in past in this research field, all the problems and challenges faces and their formulation.

Chapter 3 presents a detailed description of experimental methodologies used in our work. It involves explanation of various characterization techniques used for fabrication and characterization of devices.

Chapter 4 demonstrates the optimized growth parameters for the growth of ZnO nanostructures and discusses the effect of KMnO₄ concentration during hydrothermal growth of ZnO on the hybrid photodetector for visible light detection. It also highlights the MDMO-PPV film coating steps and its effects on the device performance. All the results and parameters obtained are discussed in detail in this chapter.

Chapter 5 concludes the work described in the thesis and further, the future scope of work has been discussed.

Chapter 2

Review of Past Work and Problem Formulation

The earliest devices developed made use of single crystal Silicon wafers. In second generation devices, challenges like reduction in energy and production cost led to adoption of alternate manufacturing technologies and Amorphous and polycrystalline Si, CdTe, CIGS were utilized. Further with aim to increase efficiency and utilize abundant and non toxic materials, organic semiconductors, perovskite materials etc., came into picture. Issues like insufficient charge extraction, low absorption, inferior mobility and morphology of organic semiconductor and device configuration in hybrid photodetectors has been a problem of prolonged research. With the aim of developing high performance hybrid photodetectors, all these issues have been thoroughly investigated till date. The researchers around the world have dealt with these issues either by synthesizing novel semiconductor materials or through modifications in device geometry. Wang et al were the first to demonstrate P3HT: CdSe nanowires heterojunction photodetectors on silicon and flexible substrates, exhibiting a greatly enhanced photocurrent, a fast response, and a recovery time shorter than 0.1 s because of the high hole-transport rate of P3HT, the high electrical conductivity of CdSe NWs. The basic motive behind these innovations has been improvement in the efficient generation of photocurrent. Therefore, several research possibilities lies in studying the structural modification of inorganic nanostructures inside hybrid photodetectors and subsequently gained insight can be best utilized for improving the functionality of these devices.

While fabricating these devices, major points to be considered are review of cost controlling factors, possible removal of costly components, search for more amicable solutions, fabrication of more industrially viable device architectures.

Chapter 3

Materials, Experimental Methods and Characterization

This chapter deals with the brief overview of the materials employed in the presented research work. Further, it gives description of various techniques pertaining to fabrication and characterization of the devices. The discussion involves the fabrication process of devices followed by description about the used characterization tools.

3.1 Materials

The selection of a material is important to fulfill the criteria for efficient device fabrication. The physics of the device is controlled by the material properties. It is important to study the optical and electrical properties of the material prior to its application. Only those materials can be selected for an active layer which satisfy the required condition of energy band gap, energy levels and its type either donor or acceptor. The other properties like surface tension, solubility, melting point and evaporation are very important when solution processed device fabrication techniques are used. For the design of hybrid photo-detector it is important to select the material which is capable of both the excitons splitting and charge transfer.

3.1.1 ITO (Indium Tin Oxide)

ITO coated glass (Indium tin oxide coated glass) belongs to the group of TCO (transparent conducting oxide) conductive glasses. An ITO glass has a property of low sheet resistance and high transmittance. The physical properties specified by the manufacturer are: 1) a sheet resistance of 15-25 Ω ; 2) an ITO layer thickness between 80 and 120 nm; and 3) a transmittance greater than 78 %. It is mostly used in research and development. ITO coated glass substrates are widely used to organic/inorganic heterojunction solar cells, Schottky solar cells, CdTe solar cells and other various thin film solar cells as transparent semiconductor oxide electrode materials since their transparency and high conductivity. ITO coated glass is most commonly used substrate for making samples because of its flatness, rigidity and its transparency in the spectral

range of interest, i.e. visible and near-infrared. It has a high work function of 4.8 eV [19]. Since ITO has high atmospheric stability and insolubility, it can be used in wet processing conditions during cleaning and spin coating.

Figure 3.1 Rectangular ITO Glass slide

3.1.2 ZnO (Zinc Oxide)

ZnO is an interesting semiconducting material owing to its huge morphological diversity such as nanorods, nanosheets, nanowire arrays, nanopencils, tower-like structures, nanobelts, nanosprings, nanocombs, and nanorings [20] (see Figure 3.2(a) and (b)). ZnO is a wide-band gap semiconductor of the II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type. ZnO nanostructures have been already utilized as active components in diverse technological applications such as, field effect transistors (FETs) [21], light emitting diodes (LEDs) [22], gas sensors [23], ultraviolet (UV) photodetectors [24] and solar cells [25].

Properties of ZnO:

Because of its many unique properties, there has been an overwhelming amount of research studies dedicated to ZnO and its applications in a wide arrange of scientific fields. One of the most attractive properties of this semiconductor is its wide band gap of \sim 3.37 eV at room temperature. A semiconducting material with a wide band gap has the ability to be effective during processes at high temperature and power, and also with operations applying large electric fields.


Figure 3.2(a) Different morphologies of ZnO, (b) Collection of ZnO hierarchical and higher order nanostructures

Moreover, there has been a recent interest in the field emission characteristics of ZnO. Other desirable characteristics of ZnO include its near UV emission, large Exciton binding energy around 60 meV that allows sufficient excitonic emission within the UV range at 298K, visible light transparency, transparent conductivity and piezoelectricity, biocompatibility, structure and property controllability, and simplicity of synthesis process. ZnO has very good electron mobility (205 cm²V¹S¹).

ZnO Crystal Structures:

ZnO can take on three of the following crystal structures: wurtzite, zinc blende, and rocksalt. ZnO crystallizes into the rocksalt (NaCl) structure at relatively high pressures, while the zinc blende ZnO structure exists only upon growth on substrates with the proper cubic lattice. The most thermodynamically stable structure for ZnO, however, is the wurtzite structure. The wurtzite structure has a hexagonal unit cell and lattice parameters a = 0.3296, and c = 0.52065 nm, where the O^{2-} and the Zn²⁺ create alternating planes of tetrahedral coordinated units as schematically shown in Figure 3.3.



Figure 3.3 Wurtzite crystal structure of ZnO

Generally, the electrical properties of ZnO are related to the crystal defects in its structure $(Zn_i; V_{Zn}; V_O; O_i)$. ZnO is intrinsically an n-type semiconductor hence it is commonly used as electron acceptor. Electron doping in ZnO is attributed to Zn interstitials (Zn_i) , oxygen vacancies (V_O) , and hydrogen [27]. The n-type intrinsic defect levels lay 0.01-0.05 eV below the conduction band shown in Figure 3.4. ZnO generally exhibit a good optical transmission (over 80%) in the visible and near infrared wavelength range due to its wide bandgap energy.

Growth Techniques of ZnO Nanostructures:

Several methods have been developed to fabricate the ZnO nanostructures. ZnO nanostructures can be grown either in solution or from gaseous phase. Typical nanostructure fabrication techniques are electro deposition, spray pyrolysis, hydrothermal

technique, sol-gel process, pulsed laser deposition, sputtering, vapor phase transport, physical vapor deposition, chemical vapor deposition, metal organic chemical vapor deposition (MOCVD).



Figure 3.4 Energy bands of defects in ZnO

Hydrothermal growth technique is a solution phase synthesis i.e. the growth process is carried out in a liquid. Hydrothermal synthesis is carried out in aqueous solution and the growth temperatures are less than the boiling point of water. Hydrothermal growth of ZnO nanostructures on the substrates starts with the deposition of the seed layer which is followed by the growth of nanostructures within a precursor solution. Hydrothermal synthesis is of considerable interest since it is environmentally friendly, has low production cost and involves low fabrication temperature. Low growth temperature is an advantage for fabrication over flexible substrates [28].

3.1.3 MDMO-PPV

The conjugated polymer used in this study is Poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1, 4-phenylenevinylene] (MDMO-PPV). MDMO-PPV is a conjugated polymer that in combination with nanoparticles, molecules, etc has been widely investigated bulk hetero junction for understanding physics of hybrid devices. The low electron affinity and superior ability to transport holes make MDMO-PPV the best Donor material. Figure 3.5 (a-b) shows the chemical structure and the energy level diagram of MDMO-PPV respectively.



Figure 3.5 (a) Chemical structure of MDMO-PPV (b) Energy band diagram

The main advantages of the use of conjugated polymers as active materials in devices are cost effective thin film fabrication methods on any substrates, light weight and mechanical strength suitable for flexible devices. It is a Light-emitting, conjugated polymer. Processability and film-forming properties found to be superior to MEH-PPV. MDMO-PPV shows solubility in toluene, xylene, THF, chloroform, chlorobenzene, cyclohexanone [16].

3.1.4 Silver (Ag)

The noble metal Ag is often used the counter electrode in hybrid photo-detector which has a work function of 4.7 eV and is deposited by thermal evaporation (melting point: 962° C).

3.2 Hybrid Photodetector Fabrication

The fabrication of the used devices is described step by step here. All processes were done in a generally clean environment and extra care has been taken so that only a minimum number of particles and impurities contaminated the samples.

3.2.1 Substrate Preparation

Patterning and cleaning of ITO

ITO-coated glass with sheet resistivity of $15\Omega/sq$ was used as substrates. ITO functions as electron collecting bottom electrode. ITO coated glass was first cut using a diamond tip glass cutter into size of 1.5×1.5 cm² and then was subsequently etched to pattern the substrates. The slides were covered with Teflon tape, leaving exposed the ITO that was to be removed with etchant. The etchant solution consisted of 10-15 mL hydrochloric acid and deionized water in 1:1 ratio. In this Solution Zn dust was added, and the glass slide was added to the solution for 30-60 seconds. The glass slide was then moved to a beaker of tap water to rinse off any remaining etchant, and the Teflon tape was removed. Finally, the etching was verified with resistance measurements. This process allows for the fabrication of multiple devices on a single ITO substrate. Each substrate had four devices with area of 0.04 cm². Since the cleaning of substrates is critical for device performance, these substrates were cleaned to remove inorganic and organic impurities clinging to their surface. The substrates were cleaned in sequential ultrasonic baths of distilled water, acetone, and iso propanol (10 min each). The cleaned substrates were then dried and placed in desiccators.



Figure 3.6 schematic of ITO Patterned glass substrate

3.2.2 Hydrothermal Growth of ZnO Nanostructures

The hydrothermal processing is a non conventional method to obtain nanocrystalline inorganic materials. The hydrothermal technique is becoming one of the most important tools for advanced materials processing, particularly owing to its advantages in the cost effective and low temperature processing of nanostructure materials for a wide variety of technological applications. Here, ZnO nanostructures were prepared by a two-step hydrothermal process consisting of deposition of a uniform and dense seed layer of ZnO on the desired substrate, followed by subsequent immersion of the substrate into a chemical bath for the growth of nanostructures of ZnO.

Seed layer deposition: 5 mM equimolar solution of zinc acetate [Zn (CH₃COO)₂, Sigma-Aldrich, 99% purity] and ethanolamine was prepared in 2-methoxyethanol and spin coated on a clean and patterned ITO coated glass substrate at a spin speed of 1500rpm for 30 seconds and annealed to 250°C in an oven.

Growth of ZnO Nanostructures: The seeded substrates were then immersed in precursor solution containing equimolar solution of zinc nitrate hexahydrate [Zn (NO₃)₂6H₂O, Sigma-Aldrich, 99% purity] and hexamethylenetetramine (HMTA, Sigma-Aldrich, 99% purity) in 25 mL distilled water mixture that was prepared in a beaker. Initially, an Apex series balance (APX-60, Denver instrument) was used to measure the desired amount of chemicals and then the beaker was sealed by aluminum wrap and was stirred using a stirrer for 5-10 min at room temperature. The growth process was carried out at temperatures (100°C) for 6 hrs. This solution was kept in a closed bottle to prevent the water evaporation during growth. A schematic of the growth setup used in our work is shown in Figure 3.7.

Firstly, the reaction of HMTA and water (H₂O) occurs and gives ammonia (NH₃) into the solution. The decomposition kinetics of HMTA into formaldehyde (HCHO) and ammonia (NH₃) have been investigated and found to be pH dependent. This process leads to hydroxide ion formation as a result of the decomposition of HMTA, which later reacts with the Zn^{2+} ions to form ZnO crystals. Ammonia (NH₃) reacts with water and this

reaction results in the formation of ammonium (NH^{4+}) and hydroxide ions (OH^{-}). Finally, these ions react with Zn^{2+} ion to form ZnO [29].



Figure 3.7 Schematic of ZnO Hydrothermal growth process

3.2.3 Deposition of MDMO-PPV Film

Spin Coating

The most widely used technique for fabrication of organic polymer based device is spin coating. The spin coating unit consists of a rotating chuck capable of rotation at various speeds and a vacuum pump. The vacuum pump is connected to the rotating chuck for holding the substrate during rotation. In a typical spin coating process the defined volume of the solution is dispensed on the substrate and the substrate is uniformly rotated with certain speed. During rotation the centripetal acceleration will cause the fluid to spread, and eventually off, the edge of the substrate leaving to form a homogenous thin film of the material on the surface of the substrate, spin coating experiment is illustrated in Figure 3.8. The thickness and properties of the deposited film commonly depends on spin

speed, viscosity, and concentration of the coating materials. The film thickness d obtained can be expressed by the following equation:

$$d = k\omega\delta \tag{3.1}$$

Where ω the angular velocity, k and delta is are empirical constants related to the physical properties of the solvent, solute and the substrate, δ has a value of around -0.5 and the constant k contains various parameters like the initial viscosity of the solution. In this study, the deposition of MDMO-PPV onto ZnO layer on ITO coated glass substrates was carried out by spin coating the respective solutions. The thickness of the layers was controlled by the spin speed (600-1200 rpm). The exact rpm and the corresponding Film thickness obtained in each case are discussed in the respective chapters under device fabrication section. Apex spin coater is used in this work.



Figure 3.8 Schematic of Spin coating

3.2.4 Deposition of Ag Electrode

Physical vapour deposition is a commonly used method for depositing metallic, metal oxide, and low molecular weight organic films on various substrates. In principle thermal evaporation is a very simple process. A ultra-high vacuum (usually 10⁶ mbar to 10⁷ mbar) is created inside the deposition chamber and the boat or filament made up of high resistance material (such as tungsten(W), molybdenum (Mo) etc.) is heated up until the material (e.g. Al, Ag) evaporates and condenses on the substrate (see Figure 3.9). The ultra-high vacuum is needed to avoid interactions between the evaporated material and impurities. The deposition rate can be controlled on varying the power supplied to the

heat source (boat) while thickness and deposition rate are monitored by oscillation quartz sensor. This method is a good choice, when gentle impact on the surface is wanted which correlates with the evaporation rate. The counter electrode (Silver 40-50nm) of the hybrid photo-detectors was deposited.



Figure 3.9 Schematic of Physical vapour deposition system



Figure 3.10 Instruments used in fabrication of device

3.3 Thin Films and Device Characterization Techniques3.3.1 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a non-destructive method of probing the electrical properties of materials. Light is focused onto the sample where it is absorbed in a process called "photo-excitation". As a result of the excess energy caused by photo-excitation, electrons jump to permissible excited states. When these electrons move back to their equilibrium states the excess energy is released through emission of light with energy equal to the energy difference between the equilibrium and excited states. This emitted light is then focused and collected by a photon Detector through a spectrometer. Much useful information can be extracted out of PL spectra:

1) **Bandgap** determination: The most common radiative transition in semiconductors is between the states in the conduction and valence bands, which equals to the energy gap of the semiconductor.2) Impurity levels and defect **detection**: Radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects.3) Recombination mechanisms: When the electrons return to their equilibrium states, also known as "recombination", both radiative and non-radiative processes can occur. The intensity of the PL peak and its dependence on the level of photo-excitation and temperature is directly related to the dominant recombination process [30]. To investigate the optical characteristics of ZnO nanostructures, photoluminescence (PL) measurements were performed using a Dongwoo PL system at an excitation wavelength of 325 nm. All measurements were conducted at room temperature. The schematic of PL measurement system is shown in Figure 3.11

3.3.2 UV-Vis Absorption Spectroscopy

When electromagnetic radiation (light) interacts with matter during which various processes can occur such as reflection, scattering, absorbance, transmittance and fluorescence/phosphorescence.



Figure 3.11 Schematic of PL measurement system

Photon absorption by matter causes its energy content of the molecules (or atoms) to increase. In general, the total potential energy of a molecule can be represented as the sum of its electronic, rotational and vibrational energies. The wavelength of light absorbed is equal to the energy required to excite an electron from a lower energy level to a level of higher energy. The principle of operation of a typical UV-Vis Spectrophotometer is shown in Figure 3.12. When the light is irradiated on a sample, it passes through or gets reflected, therefore the amount of light absorbed is the difference between the incident radiation (Io) and the transmitted radiation (I). Quantitatively absorbance is described by Equation:

$$A = -log(T) - log(I/I_o)$$
(3.2)

In the above equation, A is absorbance, T is transmittance, I_0 and I are the intensity of the incident light and the transmitted intensity respectively at a given wavelength. The absorbance A of a material is a dimensionless. In general a UV-Vis spectrophotometer comprises of a tungsten-halogen or deuterium lamp to generate the radiation, a dispersion device and a detector, which converts visible light into electrical signal. Absorption of the typical organic layers can be modeled $I(\lambda)$ using macroscopic optical quantities, which is commonly using Beers-Lambert law to correlate the layer thickness with the wavelength dependent light intensity:

$$I(\lambda) = I_{\varrho} e^{-\alpha(\lambda)d}$$
(3.3)

Where I_0 is the light intensity before injection, α is the absorption constant, d is the thickness of the absorber [30, 31].



Figure 3.12 Experimental set-up of UV- Vis absorption spectroscopy

3.3.3 Scanning Electron Microscopy

A scanning electron microscopy (SEM) is probably the most widely used semiconductor characterization instrument. A schematic of a typical SEM system is shown in Fig 3.13. Electrons are emitted from a tungsten cathode either thermionically or via field emission and are focused by two successive condenser lenses into a very narrow beam. Two pairs of coils deflect the beam over a rectangular area of the specimen surface. Upon impinging on the specimen, the primary electrons transfer their energy inelastically to other atomic electrons and to the lattice. Through many random scattering processes, some electrons manage to leave the surface to be collected by a detector facing the specimen. Usually these are the secondary electrons, originated from a depth of no larger than several angstroms that are collected by the detector. A photomultiplier tube (PMT) amplifier is used to amplify the signal and the output serves to modulate the intensity of a cathode ray tube (CRT). SEM not only can provide images of the surface but also by rotating the sample, one can obtain information about the thickness of various layers in the structure (cross-sectional SEM) [30, 32]. The morphology, lengths, size and

orientation of the ZnO nanostructures used in the present study were investigated by FESEM. Characterization is performed at 5-10 kV acceleration voltage with a working distance of 1-10 mm.



Figure 3.13 Schematic of scanning electron microscope

3.3.4 XRD Measurements

X-ray diffraction employs electromagnetic waves with a wavelength on the order of one angstrom. X-ray diffraction of semiconductor thin films is generally carried out in a diffractometer. The source of the x-rays is called an x-ray tube and consists of a water-cooled copper target onto which an accelerated electron beam (up to a few 10's of keV) is impinging inside a vacuum tube. Through inelastic interactions, x-rays are emitted which can have energies as high as the beam energy. These x-rays are then filtered and collimated into a beam through the use of a monochromator consisting of nearly perfect silicon crystals placed at specifically chosen angles to permit reflection of the x-rays. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the

diffraction pattern therefore allows us to deduce the distribution of atoms in a material. The peaks in an x-ray diffraction pattern are directly related to the atomic distances. For a given set of lattice planes with an inter-plane distance d, the condition for a diffraction (peak) to occur can be found using Bragg's law:

$$n\lambda = 2d\sin\theta \tag{3.4}$$

Where θ is the incident angle, λ is the wavelength of the x-ray, and *n* is an integer representing the order of the diffraction peak. By analyzing the diffraction pattern, one can have insights into the phase composition and crystal structure of the studied materials [30, 33]. The crystal structure of the ZnO nanostructures was investigated using XRD analysis. A Rigaku D/Max-2000 PC diffractometer was employed, using CuK α radiation ($\lambda = 1.54056A^\circ$) at an X-Ray source operating voltage of 40 kV in the 2 θ range of 20-80° at a scanning rate of 2°/min.



Figure 3.14 Schematic of (a) Bragg's law and (b) XRD measurements

3.3.5 Current-Voltage (I-V) Characterization

I-V characterization is a widely used and important method to measure the efficiency of a hybrid photo-detector. Photocurrent measurement setup is shown in Figure 3.15. Electrical characteristics of the photo-detectors are measured by a Keithley 2612 sourcemeter. Current is measured under a swept voltage bias, from -5V to 5V, also, from -12 to 12V for ZnO/MDMO-PPV devices. All the devices are measured under dark first, and then measured under monochromatic light source. Systems used for characterization of semiconductor films and devices are shown in Figure 3.16.



Figure 3.15 Photocurrent measurement setup



Figure 3.16 Instruments used for device characterization

Figures of Merits of Photodetectors [34]:

Some important photo detectors performance parameters are summarized below-

Spectral Response Range: A given photo-detector operates for a specific range of wavelengths. As the incident photon is able to generate electron hole pair only if it has an energy that is greater than or equal to the bandgap energy. Hence beyond a certain

wavelength, the light will not be absorbed by the material since the wavelength of a photon is inversely proportional to its energy. Thus, a particular semiconductor material can be used only over a limited wavelength range. The upper wavelength λ_c cutoff is determined by the band-gap energy Eg of the material.

$$\lambda_c = \frac{hc}{E_g} \tag{3.5}$$

While designing the photo-detector, the primary consideration is to select the proper material that can respond to the corresponding photo signal. In this thesis, we focus on visible light photo-detectors.

Photocurrent: The electric field across the device causes the photo generated charge carriers to be swept to the respective charge collecting electrodes, thereby giving rise to a current flow in the external circuit. This current flow is known as the photocurrent (I_{ph}).

Detector Responsivity: It is defined as the ratio of the output current signal to optical power of the input signal. It is the efficiency of the device with which different wavelengths are detected. Hence the detector responsivity can be represented as:

$$R = \frac{I_{ph}}{P_o} \tag{3.6}$$

Here, I_{ph} is the photo-induced current and P_o is the incident optical power from the optical source. Its unit is A/W.

Photosensitivity (S): It is defined as of the ratio photocurrent to dark current of the device, which is defined as:

$$S = \frac{I_{ph}}{I_{dark}}$$
(3.7)

Reverse Saturation Current: It is a small current (I_0) which is generated in the circuit due to the small reverse voltage when a photodiode is reverse biased.

Chapter 4

Hybrid Photodetector Fabrication based on ZnO Nanostructures

We report the structural and optoelectronic properties of Zinc oxide (ZnO) nanostructures prepared by hydrothermal method. The morphological, structural and optical properties of the grown ZnO nanostructures were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), photoluminescence spectroscopy (PL) and UV-Vis absorption spectroscopy respectively. Upon addition of relatively small amount of $KMnO_4$ during the in-situ hydrothermal growth the nanorods were formed, further increasing the concentration led to increased diameter of these nanorods along with that concentration of precursors was varied from equimolar to non equimolar. On varying the precursor concentrations during hydrothermal growth, change in morphological structures from Nanorods to Nanopencils and Nanoplates was observed. It is demonstrated that the KMnO₄ concentration has great influence on morphology and on the alignment of ZnO Nanostructures. Effect of KMnO₄ on the optoelectronic properties of the grown nanostructures had also been analyzed. The growth parameters responsible for varied shapes and sizes of ZnO were studied. High aspect ratio is desired as material properties depend closely on it. ZnO nanostructure with optimum aspect ratio was selected and later the same was used to fabricate ZnO/MDMO-PPV based hybrid photodiode.

4.1 Introduction

Hybrid photodetectors based on heterojunction of conjugated polymers as donor materials and metal oxide acceptor materials posses number of advantages over the inorganic technologies, including potentially low costs, solution processability and flexibility. Interface plays a crucial role in hybrid photodetector performance as the photo-induced charge separation mainly takes place at the interfaces between metal oxide nanostructures and conducting polymers. Here in this work we aim towards development of organic-inorganic hybrid photodetectors utilizing MDMO-PPV as a p-type organic material and ZnO as an n-type inorganic material. ZnO is a versatile functional material having a diverse group of growth morphologies such as, one-dimensional (1D) nanorods, nanowires and nanotubes and 2D dimensional nanodisks, nanosheets, nanoplates and nanofilms. Therefore, ZnO is a promising material for hybrid photodetector and has the advantage of easy synthesis of controlled nanostructures. The physical and chemical properties of ZnO nanostructures depend not only on their composition but also on their structure, phase, size, aspect ratio, orientation, spatial arrangement and crystalline densities. Hydrothermal technique is a non-hazardous and low temperature processing method for ZnO nanostructure growth. The morphology of ZnO nanostructures obtained from hydrothermal approach is strongly influenced by experimental conditions, such as the reaction temperature, precursor concentration, pH of the solution, surfactant additives in the solution etc. In literature it has been reported that the incorporation of chemical additives can be used to alter rod morphology. There are few reports on the role of ionic additives in solution; for e.g. incorporation of potassium chloride, Potassium permanganate in the precursor solution to influence the nanorod morphology. Hence we can obtain variety of ZnO nanostructures on tuning these parameters. In present work, we have successfully grown ZnO nanorods, nanoplates, nanopencils as well as nanospheres. To enhance the lateral growth of nanorods we incorporated potassium permanganate (KMnO₄) in the growth solution and studied its effect on ZnO nanostructure growth. In this work hydrothermally grown ZnO nanostructures were utilized to fabricate ITO/ZnO/MDMO-PPV/Ag type functional hybrid bilayered visible region photodetector with high rectification ratio [35, 36].

4.2 Experimental Details

To initiate the growth from the glass/ITO substrate, ZnO seed layer was grown on the substrate. A uniform seed layer was obtained by spin coating the seed solutions on ITO coated glass substrate. After coating, the ZnO seed layers were annealed at 250°C for 5 minutes to ensure particle adhesion to the glass surface. ZnO nanostructures were then grown by dipping the substrates in a mixture of zinc nitrate hexahydrate [Zn(NO₃)₂6H₂O, Sigma Aldrich] and hexamethylenetetramine (HMTA, Sigma Aldrich) solution in 25mL

deionized (DI) water and heating at 110°,C for 6 hrs and at atmospheric pressure [36, 37]. The influence of KMnO₄ was examined by varying its concentration as 1mM, 5mM, and 10mM in the above precursor solution.

S.NO.	HMTA CONC.	Zn(NO ₃) ₂ CONC.	TEMPERATURE	DURATION
1	0.1M	0.1M	110°C	6 Hrs
2	0.05M	0.05M	110°C	6 Hrs
3	0.01M	0.01M	110°C	6 Hrs
4	0.1M	0.05M	110°C	6 Hrs
5	0.1M	0.01M	110°C	6 Hrs

Table 4.1 Sets of Variations of Growth Parameters

MDMO-PPV was used as the donor and light absorbing active material. A 1.5 wt % solution of MDMO-PPV was prepared in Chlorobenzene, and was later used for spin coating its thin film. Spin coating of MDMO-PPV was carried out at 600 rpm for 60 sec. Subsequently the film was annealed at 70°C for 15 min. All the steps were carried out in glove box [38]. Finally, Ag as top electrode (at pressure 2X10⁻⁶ mbar) was thermally deposited using physical vapor deposition system. Figure 4.1 shows the schematic of photodetector fabrication.



Figure 4.1 Schematic of Photodetector Fabrication

4.3 Results and Discussions

4.3.1 Growth and Optimization of ZnO Nanostructures

It has been well reported in literature that the aqueous solution of zinc nitrate and HMTA results in ZnO nanorod growth. HMTA is commonly used in solution-based methods to synthesize ZnO NRAs at low temperatures and it acts as a pH buffer and slow, steady source of hydroxide ions. During the ZnO nanostructure growth process, the following reactions occur:

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \tag{4.1}$$

$$NH_3 + H_2 O \leftrightarrow NH_4^{-} + OH^{-} \tag{4.2}$$

$$2OH^{-} + Zn^{++} \leftrightarrow Zn \ (OH)_2 \leftrightarrow 2H^{+} + ZnO_2^{2-} \leftrightarrow ZnO + H_2O$$

$$(4.3)$$

Firstly, the reaction of HMTA and water (H₂O) occurs and gives ammonia (NH₃) into the solution. The decomposition kinetics of HMTA into formaldehyde (HCHO) and ammonia (NH₃) have been investigated and found to be pH dependent. This process leads to hydroxide ion formation as a result of the decomposition of HMTA, which later reacts with the Zn²⁺ ions to form ZnO crystals. Ammonia (NH₃) reacts with water and this reaction results in the formation of ammonium (NH⁴⁺) and hydroxide ions (OH⁻). Finally, these ions react with Zn²⁺ ion to form ZnO. In this system, the formation of nanorods during hydrothermal growth occurs due to the differing surface energies of the polar (002) and non-polar (100) surfaces in wurtzite ZnO. The crystallographic anisotropy of ZnO results in anisotropic growth, with the highest growth rate frequently observed along the (002) c-axis. In ZnO, one end of the basal polar plane terminates with partially positive Zn²⁺ lattice points and the other end terminates in partially negative O²⁻ lattice points. HMTA being non polar chelating agent would preferentially attach to non polar facets of ZnO nanorods leading to their vertical growth [36, 39].



Figure 4.2 Schematic showing role of HMTA in promoting 1-D growth

KMnO₄ is widely known as one of the best oxidizing agents in the solution; it performs two major roles during the growth process: (a) to produce OH⁻ ions, which controls the size of nanorods and (b) to increase oxygen content in the precursor solution, which controls the orientation. Although there is a natural tendency for ZnO anisotropic growth, generation of oxygen in precursor solution can be thought as a driving force for oriented growth. The decomposition of KMnO₄ in solution greatly increased the oxygen concentration and made the oxygen largely excessive on the surface of the growth layer. The presence of high oxygen concentration was found to act as a driving force for the anisotropic development along c-axis direction with its most stable crystal habit, which improves with concentration of KMnO₄ .The overall reaction effect incorporating KMnO₄ is as follows [39]:

$$MnO_{4}^{-} + 2H_{2}O + 3e^{-} \leftrightarrow MnO_{2} + 4OH^{-}$$
 (4.4)

$$4MnO_{4}^{-} + 4OH^{-} \leftrightarrow 4MnO_{4}^{2-} + 2H_{2}O + O_{2}$$
(4.5)

In next section we will see that KMnO₄ greatly influences optical and electronic properties of ZnO nanostructures which are indeed beneficial for our device performance.

4.3.2 Structural and Optical Characterization of ZnO Nanostructures

After the growth of the ZnO nanostructures, FESEM was used to investigate different nanostructures. When non equimolar precursor concentration was used, Nanoflakes along with nanorods, dense nanorod array and pyramid shaped nanorods or nanopencils were found to be grown for 1, 5, 10 mM KMnO₄ concentration respectively. As shown in Figure 4.3 (a), randomly oriented nanorods were observed in pristine precursor solution i.e. without any addition of KMnO₄ further on analyzing the FESEM images of ZnO nanostructures it was apparent that highly uniform and densely packed arrays of ZnO nanorods with better orientation along the c-axis were successfully formed on addition of KMnO₄ in the precursor solution, as shown in Figure 4.3(b, c and d). It is clearly evident from the FESEM that the KMnO₄ concentration influences the growth of ZnO nanostructures. Apparently, when HMTA concentration is higher in solution, initially it decomposes more quickly in solution to provide sufficient OH⁻ ions to Zn²⁺. So, base of nanorods is thicker. As time goes by, supply of Zn²⁺ is limited in solution and gradually becomes exhausted. This creates imbalance between OH⁻ and Zn²⁺ which leads to the formation of incomplete shape of nanorods that we name as nanopencils.





Figure 4.3 FESEM images of ZnO nanostructures for different KMnO₄ concentrations for 0.1M HMTA and 0.05M Zn(NO₃)₂

When Zn^{2+}/OH^{-} ratio is not maintained in the solution, nanorods are not formed. In that case, OH^{-} is utilized in bridging and coordinating Zn^{2+} to form Zn-O bonds rather than forming nanorods. In figure 4.4 FESEM images show the lateral growth of nanostructures and tampered shape of ZnO nanostructure from both ends. This is due to high mismatch of Zn^{2+}/OH^{-} ratio.



Figure 4.4 FESEM images of ZnO nanostructures for 0.1M HMTA and 0.01M Zn(NO₃)₂

On the other hand, when equimolar precursor concentration was used, nanorods with different diameters were formed for 1, 5, 10 mM KMnO₄ concentrations. ZnO (NRAs) have a rod-like shape with hexagonal cross section as shown in Figure 4.5(a, b, c).



Figure 4.5 FESEM images of ZnO nanostructures for different KMnO₄ concentrations for 0.1M HMTA and 0.1M Zn(NO₃)₂

When the equimolar precursor concentration was decreased to 0.05M, dense growth of ZnO nanorods was observed with decreased diameter. The decrease in diameter of nanorods with decreased reactant concentration could be due to low super saturation of ZnO as shown in figure 4.6. In this variation, low orientation of nanorods is observed and coverage density is also low. The reason for low orientation is lattice mismatch between ITO coated glass substrate and the nanorods because ITO has cubic lattice structure whereas, ZnO has hexagonal wurtzite structure.



Figure 4.6 FESEM images of ZnO nanostructures for different KMnO₄ concentrations for 0.05M HMTA and 0.05M Zn(NO₃)₂

When the equimolar precursor concentration was further decreased to 0.01M, we observed that there was no formation of nanorods, nanospehrical structures were formed as shown in figure 4.7. The reason for this type of growth is that HMTA concentration in the solution was not maintained which hindered the axial growth of nanostructures. Also, due to very less HMTA concentration in solution, pH was also not maintained. The coverage density of nanospheres was observed to be very less.



Figure 4.7 FESEM images of ZnO nanostructures for 0.05M HMTA and 0.05M Zn(NO₃)₂

The crystalline quality of the grown ZnO films was investigated by powder XRD. The observed XRD patterns of the prepared ZnO nanostructures are presented in Figure 4.8.

The XRD data confirmed that all diffraction peaks can be indexed to ZnO with wurtzite structure (space group: p63mc (180): $a = 3:2512A^{\circ}$ and $c = 5:2109A^{\circ}$) and are in good agreement with the JCPDS file of ZnO (JCPDS 01-089-7102). No other peaks were detected within the detection limit of the XRD instrument and XRD spectra indicated that the films have polycrystalline nature with a hexagonal wurtzite structure and any other characteristic peaks corresponding to the impurities of the precursors such as zinc nitrate and zinc hydroxide were not observed in the XRD patterns. The intense and sharp peaks depicted highly orientated crystallographic growth. It was interesting to notice that with addition of KMnO₄ during hydrothermal growth, the preferred orientation of nanorods was changed from (101) to (002) and this effect has been attributed to the presence of oxygen during ZnO growth.



Figure 4.8 XRD Plots of ZnO nanostructures for different KMnO₄ concentrations and equimolar precursor concentration

The (002) peak appears with maximum intensity in KMnO₄ modified ZnO films indicating preferred orientation of the crystals along c-axis that is perpendicular to the

substrate. The other peaks corresponding to (100), (101), (102), (110), and (103) are present with low relative intensities. The relative intensity ratio of i(002), defined as:

i(002) = I(002) / [I(100) + I(002) + I(101)](4.6)

The i(002) of the NRAs grown with KMnO₄ concentration 1mM and 5mM is 0.544 and 0.61 respectively, which is significantly improved compared to that of ZnO NRAs grown without KMnO₄ modification (i(002) =0.28). However i(002) with KMnO₄ concentration 10mM is reduced to 0.44 due to tampered shape of nanorods.

Photoluminescence (PL) is an efficient tool to study the optical, electronic and structural characteristics of different materials. A room temperature PL study was carried out in order to get insight into the optical properties of the ZnO nanostructures and to investigate defect states and crystal quality of fabricated ZnO nanostructures. The room temperature PL spectrum for non equimolar and equimolar precursor concentrations is shown in Figure 4.9 and Figure 4.10 respectively. The spectrum (Figure 4.9, 4.10) is composed of an ultraviolet (UV) emission centered at about 380 nm and a broad green emission centered at about 570 nm.



Figure 4.9 PL spectra of ZnO Nanostructures for different KMnO₄ concentrations for non equimolar precursor concentration.



Figure 4.10 PL spectra of ZnO Nanostructures for different KMnO₄ concentrations for equimolar precursor concentration

The UV emission band can be explained by the near band-edge (NBE) transition of the wide band gap ZnO nanostructures, due to the recombination of free excitons through radiative recombination process. The peak at 570 nm is due to the deep level emission (DLE) related to the impurities and structural defects in the crystal (e.g., oxygen vacancies, zinc interstitials) [40]. ZnO nanostructures without KMnO₄ addition showed intense visible band emission and weak UV emission which signified the presence of severe structural defects in the sample whereas significant improvement in near band emission was observed on KMnO₄ addition. The normalized PL spectra of ZnO nanostructures indicate decrease of intensity of defect related peaks with ZnO nanorods grown in presence of KMnO₄. The edge emission for ZnO nanorods without addition of KMnO₄ lead to less pronounced visible emission indicating reduction of defect states is due to the decrease in defects related to oxygen vacancies. The oxygen

rich growth environment for ZnO nanostructures caused by decomposition of KMnO₄ resulted in lowering of oxygen vacancies related defects.

High aspect ratio of ZnO nanostructures is required for outstanding properties and applications of our proposed device. From FESEM, we confirmed that ZnO nanorods grown by using equimolar precursor concentration has most optimum aspect ratio. Also, from both the normalized P.L. spectra, it is confirmed that the ($I_{UV}=I_{VIS}$) ratio of samples prepared using KMnO₄ in equimolar precursor concentration is significantly higher than that of non equimolar precursor concentration which confirmed that lower defects were present in sample prepared in equimolar precursor concentration using KMnO₄. From XRD, we confirmed that ZnO nanorods grown by adding 5mM KMnO₄ have highest relative intensity ratio [i(002) = 0.61]. Thus, from above observations, we concluded that ZnO nanorods grown in equimolar precursor concentration and by adding 5mM KMnO₄ were most suitable for our device performance. Figure 4.11 shows the normalized P.L spectrum of ZnO nanorods grown by addition of 5mM KMnO₄ with respect to pristine ZnO NRAs.



Figure 4.11 Normalized P.L. spectra of ZnO NRAs with and without 5mM KMnO₄

It is evident from DLE that significant amount of defects have been suppressed on adding 5mM KMnO₄. Figure 4.12 shows the XRD plot of ZnO nanorods grown by addition of 5mM KMnO₄ with respect to pristine ZnO NRAs.



Figure 4.12 XRD plot of ZnO NRAs with and without 5mM KMnO₄

We have individually investigated the independent absorption spectra of ZnO NRAs, MDMO-PPV films, and combined ZnO/MDMO-PPV heterojunction. Figure 4.13 shows the UV-Vis absorption spectra of the ZnO NRAs (with and without KMnO₄ modification). ZnO mainly absorbs in the UV region with a feeble absorption extending into the visible region of spectrum. It was observed that upon KMnO₄ modification of ZnO, the absorption in the UV region became more pronounced with a significant reduction in the visible region (ranging from 400-700 nm). The absorption of ZnO in the visible range of wavelength implies that there exist larger concentration of visible defects in pristine ZnO nanorods as compared to KMnO₄ assisted ZnO growth. This clearly

shows that upon modification with addition of 5mM KMnO₄ the defect states are reduced improving the properties of the ZnO nanorods.



Figure 4.13 UV-Vis absorption spectrum of ZnO NRAs with and without KMnO₄

Figure 4.14 shows the absorption band of MDMO-PPV. It is observed that MDMO-PPV shows significant absorption in the wavelength range 420-560 nm with its peak at 500 nm. Figure 4.15 shows the absorption spectra of ZnO/MDMO-PPV heterojunction. It was observed that absorption of ZnO was minimal in the visible region and the absorption peak of MDMO-PPV lied well in the middle of the visible spectrum. This also confirms that in our hybrid device the monochromatic light (having wavelength = 490 nm) was mainly absorbed by the polymer layer, as the ZnO NRA remained practically transparent to all the wavelengths corresponding to the visible spectrum. This is particularly important as the light is illuminated from the ITO side of the device and therefore, light has to pass through the ZnO layer to reach to the overlying layers to generate excitons and hence the photocurrent.



Figure 4.14 UV-Vis absorption spectrum of MDMO-PPV film



Figure 4.15 UV-Vis absorption spectra of ZnO/MDMO-PPV heterojunction

4.3.3 Electrical Characterization of ZnO/ MDMO-PPV Device

Current-voltage (I-V) curves are the most important evaluator of photodetector function and performance. The schematic of hybrid ITO/ZnO/MDMO-PPV/Ag photodetector is shown in Figure 4.16(a) and (b) shows the energy band diagram of the photodetector to understand the working of device. Under the dark condition, characteristics were similar to the characteristic curve of conventional rectifying junction diode which means that under forward bias condition, above the built in voltage large current was observed to flow, also an exponential increase in the current was found. However, under the reverse bias condition of the photodiode, a relatively small reverse biased current was found to flow through the diode. The ideal diode current-voltage characteristic in dark was found to obey the Schottky equation for a rectifying diode in equation (1),

$$I = I_{sat} \left(e^{\frac{V}{\eta V_T}} - 1 \right)$$
(4.7)

Where, I is the diode current, I_{sat} is reverse saturation current, V is applied voltage, η is ideality factor, V_T is thermal voltage (26mV). When an incident light strikes the photodiode the curve shifts by the quantity I_{ph} as:

$$I_{total} = I_{sat} \left(e^{\frac{V}{\eta V_T}} - 1 \right) + I_{ph}$$
(4.8)

Where I_{ph} is the photocurrent and it depends on the incident light intensity. Dark current, alternatively named the diode current, refers to the current generated while the photodetector is not under illumination. As MDMO-PPV is the absorbing material in visible region it is clear that the excitons are formed in the bulk of MDMO-PPV film (Figure 4.16 (b)). These excitons then tend to undergo dissociation near the strong built in field occurring at the interface of MDMO-PPV and ZnO, thus, resulting in the generation of the electron hole pair. While the conduction band of ZnO provides energetically favorable path for the efficient extraction of the electron through the ITO electrode. From the HOMO of MDMO-PPV, holes are transported to Ag electrode.



Figure 4.16(a) Schematic of hybrid ITO/ZnO/MDMO-PPV/Ag photodetector (b) Energy level diagram with respect to vacuum level for ITO/ZnO/MDMO-PPV/Ag photodetector

We selected ZnO NRAs modified by 5mM KMnO₄ for our device and MDMO-PPV film was coated over it by two modes: i) sample was kept dipped in 1 wt% MDMO-PPV solution in chlorobenzene then 1.5 wt% MDMO-PPV solution was spin coated over it. ii) 1.5 wt% MDMO-PPV solution was directly spin coated over sample without keeping it dipped. Figure 4.17 shows the log I-V characteristics of ITO/ZnO/MDMO-PPV/Ag photodetector with ZnO growth modified by 5 mM KMnO₄ and spin coated MDMO-PPV by first mode in the dark and under green light illumination ($\lambda = 490$ nm). In absence of illumination, the dark-current is small because of the very large charge injection barrier under reverse bias. The reverse saturation current measured at -2V is 16.388 × 10⁻⁶A. Upon green light illumination using a monochromatic light source (λ =490nm) from the ITO counter electrode on ITO/ZnO/MDMO-PPV/Ag photodetector was under incident optical power (Popt) of 14.7mW/cm², photocurrent (Iph) nearly two orders of magnitude higher as compared to the dark current was found to flow through the photodiode. The Photocurrent Responsivity (R) is given by:

$$R = \frac{I_{ph}}{P_{opt}} \tag{4.9}$$



Figure 4.17 I-V characteristics of ITO/ZnO/MDMO-PPV/Ag photodetector in log scale

The photocurrent responsivity (R) of ITO/ZnO/MDMO-PPV/Ag photodetector was estimated utilizing the equation (4.9) (above) was found to be 2.A/W at -2V which is quite high, and this clearly indicates enhanced photo response under green light (490 nm) illumination. This rise in photocurrent is attributed to cumulative effect of high absorption coefficient of MDMO-PPV film in visible region which led to generation of large number of excitons, higher ZnO/MDMO-PPV interface area for exciton dissociation and low defect concentration of ZnO NRAs modified by 5mM KMnO₄. Highly oriented and dense ZnO NRAs achieved by addition of KMnO₄ facilitates large interface area of ZnO/P3HT leading to more efficient dissociation and increased photocurrent. The photosensitivity S is given by:

$$Photosensitivity = \frac{Photocurrent-Dark current}{Dark current}$$
(4.10)

Photosensitivity was calculated to be 128 at -2V and highest photosensitivity was reported to be 335 at -0.24V. The rectification ratio calculated from dark I-V characteristics was 26 at \pm 2V. But the observed value of the rectification ratio of the photodetector (under dark condition) was not very high as would have been expected from highly oriented KMnO₄ assisted ZnO NRAs. The reason for low value of rectification ratio was attributed to incomplete capping of ZnO NRAs by overlying spin

coated MDMO-PPV, which might result in direct contact between the ZnO nanorods with the top electrode, thus providing leakage pathways in the photodetector also the two step mode by which MDMO-PPV film was coated seem to create same solvent effect as the sample was kept dipped in same solution for a period of time before spin coating. In order to circumvent these problems, we made sure there were no or negligible pinholes present during seed layer coating of ZnO over ITO to avoid any leakage pathway during current flow. We also modified the coating process of MDMO-PPV by making it one step process i.e. directly spin coating MDMO-PPV film without keeping the sample dipped. Figure 4.18 shows the log I-V characteristics of ITO/ZnO/MDMO-PPV/Ag photodetector after modification.



Figure 4.18 I-V characteristics of ITO/ZnO/MDMO-PPV/Ag photodetector in log scale

The rectification ratio calculated from I-V characteristics is 466 which is quite large and is 18.6 times higher than the previous obtained result. Reverse saturation current is significantly reduced to 3.03μ A at -12V. Due to better coating of MDMO-PPV film, photocurrent was measurable upto higher voltage. Hence, the hybrid device that we have
fabricated could be used for different range of voltages depending upon the applications. Photoresponsivity (R) of ITO/ZnO/MDMO-PPV/Ag photodetector was estimated utilizing the equation (4.9) and was found to be 2.69A/W at -12V which is also quite high. There is significant improvement in photosensitivity which was reported to be 547.2 at -12V and highest photosensitivity was obtained to be 707 at -1.49V. Another I-V response was obtained at the same bias voltage of $\pm 12V$. High rectification ratio 466 was reported and photosensitivity obtained was of three orders at 6923. It was improved by almost 10 times from the previously obtained result. The Photoresponsivity was increased to 3.7A/W Figure 4.19 shows the log I-V characteristics of ITO/ZnO/MDMO-PPV/Ag photodetector.



Figure 4.19 I-V characteristics of ITO/ZnO/MDMO-PPV/Ag photodetector in log

scale

The enhancement in the photosensitivity in device with ZnO (5 mM) is attributed to the lower defect density and more aligned and compact ZnO NRAs and better MDMO-PPV film formation by directly spin coating it, thus resulting in large interface area between ZnO/MDMO-PPV which resulted in more dissociation sites for photogenerated excitons. In table 4.2 the calculated parameter values of ZnO/MDMO-PPV photodetector are summarized:

Device structure	Dark	Photo-	Max. photo-	Photocurren	Reverse
	Rectificati	sensitivity	sensitivity	t	saturation
	on ratio			responsivity	current
ITO/ZnO/MDMO-	118	128 (-2V)	335(-0.24)	2.22A/W	16.4µA
PPV/Ag					
(on dipping)					
ITO/ZnO/MDMO-	466	547(-12V)	707(-1.48V)	2.9A/W	3.05 µA
PPV/Ag					
(without dipping)					
ITO/ZnO/MDMO-	466	712(-12V)	6923(-1.48V)	3.7A/W	3.05 µA
PPV/Ag					
(without dipping)					

Table 4.2: Parameters of fabricated ITO/ZnO/MDMO-PPV/Ag Photodetector

Chapter 5

Conclusions and Future Scope of Work

5.1 Conclusions

In this work, we have demonstrated the fabrication and characterization of inorganicorganic hybrid photodetector for visible light photodetection. ZnO was a suitable candidate for our work as it has the ability to show varied morphological diversity along with promising material properties. We have grown nanorods, Nanoflakes, nanopencils and nanospheres in our work. In order to achieve high performance by our ITO/ZnO/MDMO-PPV/Ag device, we used highly ordered and dense array of ZnO nanorods with suppressed surface defects which were obtained by addition of KMnO₄ into zinc nitrate/ HMTA system. This reduction in defect states and increase in ZnO/MDMO-PPV interface area resulted in better charge transport and efficient exciton diffusion. The rectification ratio and Photoresponsivity of our device was further improved by modification in MDMO-PPV film coating steps. Better film formation led to better device response. For 5mM KMnO₄ concentration in the precursor solution the highest measured responsivity was under incident visible light and rectification ratio was 466. As per our knowledge we have achieved the highest rectification ratio, responsivity of the ZnO/MDMO-PPV bilayered photodiode in this configuration.

The major conclusions of this work are as follows:

- The key requirement to bring substantial improvement in device performance is large donor acceptor interface. Optimization of highly oriented ZnO nanorod array with suitable aspect ratio is critical in this regard.
- Optimization of ZnO nanorods was possible by the addition of KMnO₄, a strong oxidizing agent in the solution which played major role in tuning the structural, optical and electronic properties of ZnO nanorods.
- MDMO-PPV showed excellent absorption in visible light spectrum and coating a good film of MDMP-PPV enhanced the performance of our device.

5.2 Future Scope

The carried out research work has highlighted the importance of interfaces and morphology of ZnO nanostructures in the context of hybrid photodetector performance. Future scope lies in further improvement and engineering of material properties to enhance sensitivity and responsivity of photodetectors. Another future scope lies in developing more engineered and advanced techniques for defect free growth of novel ZnO nanostructures in order to control their optical and electronic properties for improved device performance. In this work, our photodetector was tuned to one wavelength (λ =490nm). Future scope lies in further using it for dual wavelength tuning based applications like optical switch. As we know that ZnO absorbs in UV region and MDMO-PPV absorbs in visible region of light spectrum, two wavelengths can be tuned together for other application.

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